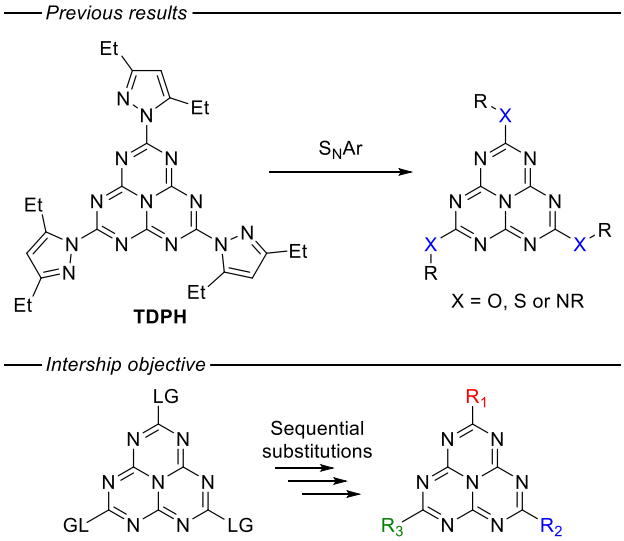
M2 Internship (6 months): Control of the substitution for formation of unsymmetrical heptazines.

Contact: Lucas FRÉDÉRIC, Clémence ALLAIN and Laurent GALMICHE, PPSM laboratory, ENS Paris-Saclay

(lucas.frederic@ens-paris-saclay.fr, clemence.allain@ens-paris-saclay.fr, laurent.galmiche@ens-paris-saclay.fr)

Context: This internship aims to deepen and control the number of substitution(s) on heptazine derivatives in order to investigate the influence on optical properties (absorbance and emission through fluorescence). Heptazines have recently received a renewed interest for their potential applications in various domains such as photocatalysis,[1] liquid crystals,[2] metal and covalent organic framework[3] or optoelectronics.[4] Promising results have already been reported, however the number of available starting materials remains limited and restricts the possibility of functionalization.



In this project, we propose to give guidelines for the synthesis of unsymmetrical heptazines, and to rationalize the impact of this symmetry breaking to optical properties of the molecules. So far, the PPSM team has established the synthesis of a new key intermediate named TDPH in order to form homo-trisubstituted heptazines under mild conditions. Series of molecules have been synthesized in the laboratory with peculiar optical properties. In this context, the objectives of this internship will be 1) develop new synthetic methodologies to obtain and characterize unsymmetrical heptazines 2) explore optical properties of these new molecules, principally with UV-vis absorbance and fluorescence emission.

The candidate should possess strong skills in organic chemistry as well as common characterization of organic materials. A background in photophysics would be an asset but is not mandatory.

If you are interested, please refer to contacts above.

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[1]Wang X, Maeda K, Thomas A, Takanabe K, Xin G, Carlsson JM, et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nature Mater* **2009**;*8*:76–80. https://doi.org/10.1038/nmat2317.

[2] Mir Sayed S, Deng L-L, Lin B-P, Yang H. A room-temperature heptazine core discotic liquid crystal. *Liquid Crystals* **2017**;*44*:2175–83. https://doi.org/10.1080/02678292.2017.1371343.

[3]Luebke, R.; Weseliński, Ł. J.; Belmabkhout, Y.; Chen, Z.; Wojtas, Ł.; Eddaoudi, M. Microporous Heptazine Functionalized (3,24)-Connected Rht-Metal–Organic Framework: Synthesis, Structure, and Gas Sorption Analysis. *Crystal Growth & Design* **2014**, *14* (2), 414–418. https://doi.org/10.1021/cg401802s.

[4]Li, J.; Nomura, H.; Miyazaki, H.; Adachi, C. Highly Efficient Exciplex Organic Light-Emitting Diodes Incorporating a Heptazine Derivative as an Electron Acceptor. *Chem. Commun.* **2014**, *50* (46), 6174–6176. https://doi.org/10.1039/C4CC01590H.